

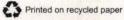
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User's Guide UG-2035-ENV

NATURAL ATTENUATION GENERAL DATA GUIDE

February 1999

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EXECUTIVE SUMMARY

This guide presents data requirements and methodologies used to evaluate the potential for using natural attenuation as a remedial option at sites contaminated with fuel hydrocarbons and chlorinated solvents. This document is aimed at users who: (i) want to analyze site-specific data that they have in hand in terms of natural attenuation; (ii) are just initiating the site characterization, and (iii) would like to collect data that could be used to implement natural attenuation. Users who have data in hand can identify additional parameters, methods, and interpretations that are necessary to complete the process. For sites that have not yet been characterized, the guide can be used to work through the process of identifying data needs, methods for data collection, analysis, and interpretation.

One of the critical determinations that the user will be required to make is the status of the plume. The user must determine whether the plume is contracting, stabilizing, or expanding. More specifically, the user must demonstrate to regulators that the plume in question does not and will not pose a threat to either human or ecological receptors. Once the parameters that control plume dynamics and contaminant fate are delineated, e.g., hydraulic conductivity, adsorption and biodegradation, the user can use this guide to select parameters for long-term monitoring that most appropriately meet the regulatory requirements.

The guide consists of seven tables that present natural attenuation data needs from an interdisciplinary perspective. The data necessary to evaluate natural attenuation are organized into tables that are grouped into two categories: (I) Data Analysis and Quality Control and (II) Methods.

The first set of tables summarizes and interprets biogeochemical data including parameters that are often collected as part of a site assessment. Recommendations for quality control of the data are also summarized in this set of tables. Hydrogeological, biogeochemical, and contaminant data needs and direct push tools that can be used to collect these data are summarized in the second set of tables. References are presented to help the reader locate more specific information about the method or approach.

Although this guide is not all-inclusive with respect to theory and application, the tables summarize the main issues that should be taken into account when considering natural attenuation as a remedial option. The guide is intended to serve as a complimentary tool to more detailed theoretical texts currently in circulation.

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OVERVIEW

This guide is a decision-making tool to help remedial project managers (RPMs) determine whether natural attenuation can be used as a remedial option at contaminant release sites. Data requirements and methodology to evaluate the potential for using natural attenuation are presented. For sites where the natural attenuation remedial option is implemented, tables of commonly measured parameters, general data collection rationale, and interpretation guidance are included.

Natural attenuation is the reduction in contaminant concentration due to the action of natural processes. The effectiveness of these processes depends on a complex interaction between the contaminants and site specific hydrology and biogeochemistry. This guide presents data requirements and methodology that have been shown through field experience to be useful in evaluating the major parameters and the potential for implementing natural attenuation as a remedial option at sites contaminated with fuel or chlorinated solvents. Sites contaminated with heavy metals alone or in combination with other contaminants require additional characterization work that is not covered in this guide.

The information in this guide is organized into seven tables. The tables are separated into two categories ((I) Data Analysis and Quality Control and (II) Methods) that are designed to help the investigator considering natural attenuation answer the following questions:

REQUIREMENTS	LOCATION IN THE GUIDE		
Does the available data demonstrate occurrence of natural attenuation?	Category I – Tables 1 and 2		
What is the status of the plume?	Category I – Tables 1 and 2		
Have the investigation goals been achieved?	Category I - Table 3		
What should be considered when preparing the conceptual site model and monitoring and closure plans?	Category I - Tables 1 through 3		
 What site characterization data are required to determine whether natural attenuation is occurring? What are the contaminants of concern at the site? Where are the contaminants located - vadose zone, saturated zone, or both? Are the contaminants migrating? Is the plume shrinking, stable, or expanding? Are intermediate metabolites (i.e., breakdown products) detectable? 	Category II - Tables 4 through 6		
What tools are available to obtain the data necessary to achieve the project goals?	Category II – Tables 4 through 7		

HOW TO USE THIS GUIDE

Guide Contents. This guide consists of seven tables that present data interpretation and methods from an interdisciplinary perspective. Wherever possible, references are presented to help the investigator locate more specific information about the method or approach. The tables are separated into two categories: (I) Data Analysis and Quality Control and (II) Methods.

Category I

Data Analysis and Quality Control:

Table 1. Biogeochemical Data Correlations Table 2. Interpreting Multiple Parameters Table 3. Quality Control

Category II

Methods:

Table 4. Hydrogeologic Data Table 5. Biogeochemical Data Table 6. Contaminant Data Table 7. Direct Push Tools

If site characterization data are available, the user should consult Tables 1 through 3 to organize, interpret, and assess the quality of the data. This will enable the user to construct a preliminary conceptual site model and recognize additional site characterization data needs. Once a thorough site characterization has been completed, the status of the plume can be determined and a monitoring and closure plan presented to the appropriate regulatory agency. If the site has not been characterized, Tables 4 through 6 should be consulted to identify data and data collection methods.

Site Characterization/Plume Status. One of the critical determinations that the user will be required to make is the status of the plume. The user must determine whether the plume is contracting, stabilizing, or expanding. More specifically, the user must demonstrate to regulators that the plume in question does not and will not pose a threat to either human or ecological receptors. Once the parameters that control plume dynamics and contaminant fate are delineated, e.g., hydraulic conductivity, adsorption and biodegradation, the user can use this guide to select parameters for long-term monitoring that most appropriately meet the regulatory requirements.

Figure 1 is an idealized illustration of changes in the biogeochemistry of a contaminated site that occur during natural attenuation. These changes range from the anaerobic and highly negative redox potential characteristic of methanogenesis near the source to the increasingly more oxygenated and positive redox potential at the edges of the plume. The reader may find it useful to refer to this diagram as they work through their site characterization data. For example, if the site characterization data demonstrate that primarily anaerobic processes, i.e., methanogenesis or

sulfate reduction are occurring, then it is possible that the boundaries of the plume have not been identified. In this case, it would be necessary to perform additional sampling to either identify the edge of the plume or demonstrate that the contaminants are localized to this region of the plume. It should also be kept in mind that aquifers naturally rich in organic matter may be anaerobic.

Tables 4, 5, and 6 describe parameters currently evaluated in natural attenuation studies. Data flagged with an "R" are generally required and are usually independent of the site and contaminants. Data identified with an "O" are often required but will depend on site and contaminant characteristics, e.g., vinyl chloride would only be measured at a site known to be contaminated with chlorinated solvents. Data that is usually collected as part of a research program is identified as "R&D." The investigator should be aware that site interpretation is often strongly influenced by the analyses that are conducted. For example, the redox potential is a critical variable when considering natural attenuation. However, as is illustrated in Figure 1, knowing the concentrations and distributions of oxidized and reduced chemical species is critical to the proper interpretation of the redox potential. For example, even if the redox potential and hydrogen concentration are adequate, sulfate reduction will not occur in the absence of sulfate. These data are also essential for predicting the future configuration of the plume. They can be used to determine whether the concentration of alternate electron acceptors is adequate to remediate the contaminants or whether the addition of alternate electron acceptors could promote more rapid remediation.

Site Characterization Tools. Tables 4, 5, and 6 summarize the methods used to collect data included in natural attenuation studies. Direct-push tools, which are increasingly useful to investigators considering natural attenuation, are listed in Table 7. Direct-push systems are used to delineate a plume, determine hydrogeologic parameters, recover samples, and measure the concentrations of contaminants and nutrients in soil, water, and soil gas. Figure 2 illustrates a conceptual site model generated using the Site Characterization and Analysis Penetrometer System (SCAPS) site characterization data.

Data Interpretation. Table 1 lists correlations that have been observed in field data (adapted from Wiedemeier, et al., 1995). It serves as a guide for the interpretation of data sets, e.g., the concentration of dissolved hydrogen and availability of alternate electron acceptors. The conditions described in Table 1 may not apply to all sites, so interpretations should be used with caution. Table 2 lists and interprets groups of data that exhibit strong cross-correlations. Examples include hydrogen concentration and use of alternative electron acceptors and the affect of multiple hydrogeological parameters on contaminant concentration and distribution. If the user detects the types of biogeochemical changes discussed in these tables, it is highly probable that biodegradation is occurring. However, the user will still have to determine the status of the plume. This task will require knowledge of the local ground water flow gradient and hydraulic conductivity distribution. It will also be necessary to generate and evaluate electron acceptor and contaminant concentrations along the primary flow path from the source to the leading edge as a function of time.

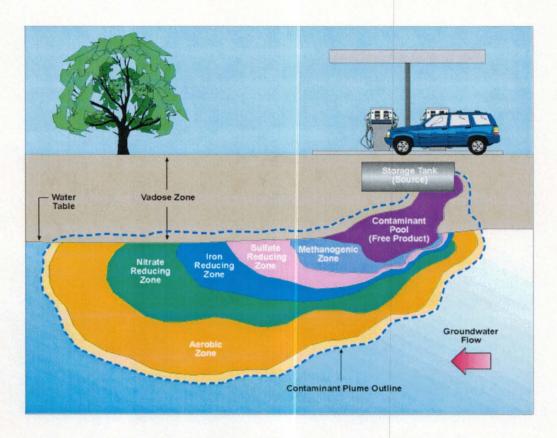


Figure 1. Idealized illustration of the spatial distribution of biogeochemical zones that may occur at a site contaminated with petroleum hydrocarbons. Prior to encountering the contaminants, the groundwater was aerobic. Following the release, bacteria depleted the oxygen near the source, generated hydrogen, and created conditions that support highly anaerobic degradation processes. As the distance from the source increases, the hydrogen concentration decreases and alternate electron acceptors are utilized. Near the plume boundary, the concentration of oxygen increases and the redox potential becomes increasingly more positive.

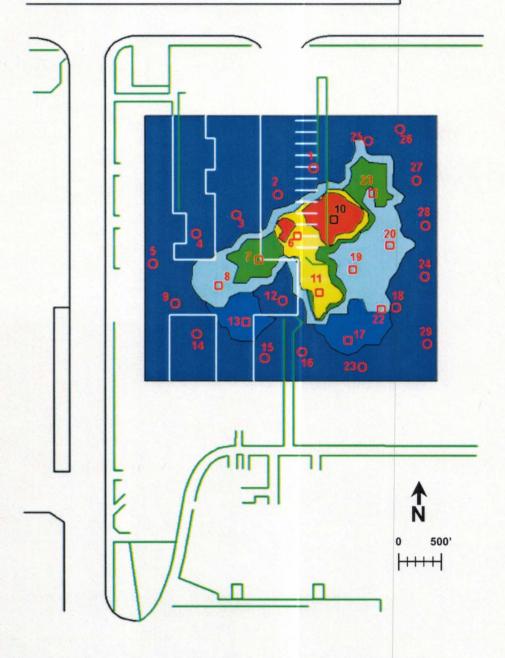


Figure 2. Example of a conceptual site model for a leaking UST. Site map was generated using laser induced fluorescence intensity collected at a depth of 12 feet bgs (capillary fringe). The colors indicate relative hydrocarbon concentrations (red>yellow>green>blue). Circles show locations of pushes that were non-detect from the surface to the aquifer. Squares mark pushes where hydrocarbons were detected. Groundwater flow is toward the southwest.

Data Quality. When considering natural attenuation, the investigator must define the current and future configuration of the contaminant plume. To ensure that this objective is achieved, Table 3 refers to items which an investigator should use to test for inconsistencies in the data. Inconsistencies can be caused by systematic, instrumentation, or model simulation variability. They can often be recognized by anomalies in the data. For example, inconsistencies in pH or the mass balance, and negative redox potentials in strata containing high concentrations of dissolved oxygen suggest sampling problems and/or a highly heterogeneous subsurface environment.

Sampling and Monitoring Wells. Before proceeding with an investigation, careful consideration should be given to the optimal placement and design of monitoring wells. Proper placement and design of wells can save time and money and lead to more precise assessment of the site. If wells are not properly designed and installed, or are installed in less than optimal locations, site data can be unreliable and misleading. While most monitoring wells have been installed following methods outlined in ASTM 5092 (Practice for design and installation of ground water monitoring wells in aquifers), investigators may consider direct-push installation of monitoring wells (ASTM 6001). One particular advantage of these types of wells is that they can be constructed with discreet screen or sampling port depths. This allows for better delineation detail in three dimensions than conventional monitoring wells. Multi-purpose wells should also be considered. For instance, wells located in regions of the plume requiring monitoring during one phase may (if the plume expands) require remediation at a future time. In these cases, a little forethought can result in significant cost savings.

APPLICABILITY

Due to the relatively young nature of natural attenuation assessment and its application to the risk-based corrective action process (ASTM E1739), the user is encouraged to remain abreast of technical and political developments. While many references are presented in this guide, it is anticipated that additional publications will be forthcoming (ASTM DNA). In addition, experienced practitioners can be consulted prior to field data collection, analytical efforts, computer modeling, and conclusive decision-making. Regulatory agencies should be identified and consulted prior to proceeding with field activities to ensure that the proposed work will satisfy all regulatory requirements.

ACRONYMS

AA - Atomic adsorption
bgs - Below ground surface

DNAPL - Dense non-aqueous phase liquid

GC/MS - Gas chromatography mass spectroscopy

IC - Ion chromatography

ICP - Inductively coupled plasma spectroscopy

LIF - Laser induced fluorescence

LIBS - Laser induced breakdown spectroscopy

LNAPL - Light non-aqueous phase liquid

MPN - Most probable number
PCR - Polymerase chain reaction

SCAPS - Site characterization and analysis penetrometer system

TDR - Time domain reflectrometry

QC - Quality control

UST - Underground Storage Tank
VOC - Volatile organic carbon
XRF - X-ray fluorescence

DATA ANALYSIS AND QUALITY CONTROL

Table 1. Biogeochemical Data Correlations. General biogeochemical observations and corresponding interpretations related to natural attenuation are presented here. The information can be used to evaluate available data, construct a conceptual model, or as guidance to help determine future data needs.

SITE ASSESSMENT /OBSERVATIONS	INTERPRETATION			
Dissolved oxygen (D.O.) > 0.5 mg/L or $> 1-2\%$ by volume in the vadose zone	Aerobic biodegradation is the predominant process; end products include carbon dioxide; degradation of TCE but not PCE is reported to occur aerobically.			
D.O.< 0.5 mg/L; nitrate (NO ₃ ⁻) present at concentrations greater than 1 mg/L	Anaerobic nitrate (NO ₃) reduction is the predominant biodegradation process; nitrite (NO ₂) is an unstable intermediate product of nitrate reduction; measurable nitrite should not be present; the terminal product is nitrogen; fuel hydrocarbons are degraded; degradation of TCE under hypoxic conditions requires nitrate.			
$Fe^{2+} > 0.5 \text{ mg/L}$; D.O., nitrate and nitrite $< 0.5 \text{ mg/L}$	Anaerobic ferric iron (Fe ³⁺) reduction is the predominant biodegradation process; end product is ferrous iron (Fe ²⁺); fuel hydrocarbons, PCE and TCE are degraded.			
$SO_4^{2^-} > 1 \text{ mg/L}$; HS ⁻ > 0.05 mg/L; D.O., nitrate, nitrite and Fe ²⁺ < 0.5 mg/L	Anaerobic sulfate (SO ₄ ²) reduction is the predominant biodegradation process; end product is sulfide; fuel hydrocarbons, PCE and TCE are degraded.			
CH ₄ > 0.2 mg/L; SO ₄ ²⁻ < 1 mg/L; HS ⁻ < 0.05 mg/L; D.O., nitrate, nitrite and Fe ²⁺ < 0.5 mg/L	Anaerobic methanogenesis (methane production) is the predominant biodegradation process; end product is methane; fuel hydrocarbons, PCE and TCE are degraded.			
Dissolved hydrogen concentration; 0.2-0.8 nM	Anaerobic iron reduction predominates; in the presence of chlorinated ethenes, the end products are chloride, dichloroethene, and vinyl chloride.			
Dissolved hydrogen concentration; 1-4 nM	Anaerobic sulfate reduction predominates; in the presence of chlorinated ethenes, the end products include chloride, dichloroethene, and vinyl chloride.			
Dissolved hydrogen concentration; 5-25 nM	Anaerobic methanogenesis predominates; in the presence of chlorinated ethenes, the end products are chloride, dichloroethene, and vinyl chloride.			

Table 2. Interpreting Multiple Parameters. Natural attenuation occurs through the action of multiple biotic and abiotic processes. Thus, no single parameter is characteristic or descriptive of the entire process. However, selected parameters, when grouped together, provide insight into site-specific processes. Information in this table can also be used as input to a fate and transport computer program, to construct and calibrate a conceptual site model, and document the occurrence of natural attenuation.

DATA	INTERPRETATION
Concentrations of metabolic intermediates, e.g., dichloroethene and vinyl chloride at TCE and PCE contaminated sites or oxidized hydrocarbons, e.g., alcohols and carboxylic acids at fuel sites	Suggests that biodegradation of hydrocarbons or chlorinated solvents is occurring if known bacterial byproducts, i.e., carboxylic acids or dichloroethene and vinyl chloride are present respectively.
Dissolved oxygen (O ₂), nitrate (NO ₃ ⁻), iron (Fe ²⁺), manganese (Mn ²⁺), sulfate (SO ₄ ²⁻), sulfide (H ₂ S, HS), methane (CH ₄)	Identify electron acceptors and metabolic end products, e.g., sulfide and methane are characteristic of anaerobic degradation.
Dissolved chloride, conductivity, temperature, salinity	Verify that samples were obtained from the same ground water system, i.e., conductivity, temperature and salinity should be similar for samples from the same aquifer; chloride may be used to estimate extent of chlorinated solvent degradation.
Dissolved Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Cl ⁻ , Br ⁻ , PO ₄ ³⁻ , inorganic carbon, temperature.	Determine whether adequate nitrogen and phosphorus are available to support microbial activity; indicate analytical accuracy via mass balance of major cations and anions (molar quantities should be within 10%).
Alkalinity, hardness, pH, salinity, and soluble Fe inside and outside the contaminant plume	Identify site-specific geochemical processes that may regulate the rate/extent of natural attenuation; extremes of pH or salinity may inhibit microbial activity; an abrupt increase in Fe ⁺² suggests biodegradation is occurring.
Total iron Fe(II) - ferrous iron Fe(III) - ferric iron	Identify the potential for anaerobic hydrocarbon degradation; Fe(III) is reduced and transferred from aquifer minerals to soluble Fe(II); lower pH (under reducing conditions) contributes to ferric iron dissolution; soluble iron concentrations tend to decrease rapidly downgradient of the hydrocarbon plume as ferric and ferrous iron are oxidized to insoluble products by dissolved oxygen.
Soil bulk density, porosity, contaminant partition coefficient, dispersion coefficients, total organic carbon, soil moisture in the vadose zone, and biodegradation rates	Estimate extent of contaminant migration since date of release; model contaminant fate and transport; determine whether moisture present in the vadose zone to support microbial activity is adequate.
Fate and transport models	Display conceptual models and site characterization data; evaluate location of potential receptors; determine source area locations; predict concentrations of nutrients and contaminants at points of concern; demonstrate extent of natural attenuation; estimate time required for contracting or expanding plume to reach a particular configuration; aid in selection of monitoring points; evaluate remediation options.

Table 2. Interpreting Multiple Parameters (Continued)

DATA	INTERPRETATION			
Ratio of ¹² CO ₂ / ¹³ CO ₂	Monitor biodegradation of pollutants; petroleum hydrocarbons contain less carbon-13 than do calcareous minerals; an increase in this ratio compared to an uncontaminated background sample suggests that biodegradation is occurring.			
Soil gases	Evaluate subsurface biological processes; evaluate progress of biodegradation, e.g., the use of alternate electron acceptors is regulated by the concentration of soluble hydrogen.			
Water soluble stable isotopes (¹⁸ O/ ¹⁶ O, ² H/ ¹ H, ⁸⁷ Sr/ ⁸⁶ Sr)	Identify water sources; verify that samples were collected from same ground water system.			

Table 3. Quality Control. The user must ensure that the data are consistent. This table contains recommendations for ensuring that samples are collected from the performance, and assuring analytical accuracy.

RECOMMENDATION	RATIONALE
Perform cation/anion mass balance	Indicates analytical accuracy via mass balance of cations and anions (molar quantities should be within 10%).
Determine whether pH is consistent with respect to geochemical parameters, e.g., oxidation state	Indicates analytical accuracy; identifies sampling errors; can help identify chemical and environmental transition zones, e.g. changes in pH may be associated with microbial activity.
Implement model validation efforts	Indicates predictive capability of chemical fate and transport model; at least one validation phase should be implemented each time a model is used.
Conduct model sensitivity analyses	Indicates which variables are most influential over the predictive results of the chemical fate and transport model; variables causing most influence over the model predictive capability should be measured with greatest accuracy and precision; a model can never be stronger than its' weakest assumption.
Conduct geostatistical analyses	Assists with determination of spatial and temporal variability of data such as aquifer hydraulic conductivity, geologic controls and chemical concentrations; determines most costeffective locations for sample collection by characterizing the precision of experimental design options; helps characterize the precision of ground water model site representations and fate and transport predictions; allows for interpolation of values between data points of known certainty and determine the errors associated with the interpolation. An on-line introduction to geostatistics, including demo software can be found at http://www-sst.unil.ch/geostatistics.html.
Ensure analytical equipment quality control steps followed	Identifies errors introduced by equipment variability, improper storage, inadequate transport conditions, and operator inconsistencies.
Ensure field quality control steps followed	Identifies errors introduced by equipment variability, operator inconsistencies, sampling inconsistencies, and improper sampling protocol.

METHODS

Table 4. Hydrogeological Data. This table summarizes physical processes that affect contaminant dynamics in the vadose and saturated zones. Parameters that are usually required are identified with an "R". Parameters that are contaminant and/or site specific are identified with an "O".

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES
Direction and gradient of ground water flow	Delineate piezometric surface using water table elevations measured from monitoring wells and/or piezocone data; conduct aquifer pumping or slug tests; flowpath modeling	Estimate rate and direction of plume migration	R	ASTM D4075; ASTM D5730; ASTM D5778; ASTM D6000; ASTM D6067; ASTM PS64; ASTM PS85; EPA 1988; EPA 1993a,b, and d; Freeze and Cherry, 1979; Gilbert, 1987; Nielsen, 1991; Bardossy, 1992
Hydraulic conductivity (saturated and vadose zone)	Conduct aquifer pumping or slug tests; run piezocone dissipation tests; conduct vadose zone permeameter and infiltrometer tests; tensiometer tests; evaluate soil moisture content and characteristic curves to determine unsaturated hydraulic conductivity	Estimate rate of plume migration; define zones of conservative migration	R	ASTM D2325; ASTM D3017; ASTM D3152; ASTM D3404; ASTM D4043; ASTM D4044; ASTM D4050; ASTM D4075; ASTM D4643; ASTM D4944; ASTM D4959; ASTM D5084; ASTM D5126; ASTM D5220; ASTM D5298; ASTM D5730; ASTM D6067; Everett et al., 1984; Nielsen, 1991; Wilson et al., 1995
Vadose zone moisture content	Evaluate by use of neutron probe; TDR probe; tensiometer; calcium carbide gas pressure test; direct heating	Estimate vadose zone hydraulic conductivity; microbial moisture requirements	R	ASTM D2216; ASTM D3017; ASTM D4643; ASTM D4944; ASTM D4959; ASTM D5220; EPA 1984; EPA 1993a and b; Everett et al., 1984; Wilson et al., 1995

Table 4. Hydrogeological Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIE R	REFERENCES
Lithology	Evaluate by field logging; cone penetrometer tests; piezocone strain gauge and pore pressure dissipation tests; geophysical properties, engineering properties; structural geology; soil density tests, permeametry; aquifer pumping and slug tests; hydraulic conductivity; piezometric surface mapping	Identify preferential flow paths, confining layers, and potential for vertical migration	R	AGI, 1989; ASTM D420; ASTM D421; ASTM D1452; ASTM D1586; ASTM D1587; ASTM D2325; ASTM D2488; ASTM D3152; ASTM D3385; ASTM D3404; ASTM D4083; ASTM D4220; ASTM D4643; ASTM D4700; ASTM D5730; ASTM D5730; ASTM D5778; ASTM D6044; ASTM D6051; ASTM D6067; Clark, 1988; Driscoll, 1986; EPA, 1988; Gilbert, 1987; Nielsen, 1991; Wilson et al., 1995
Depth to ground water	Measure in the field using wells; pressure transducers; piezocone measurements; geophysics	Estimate volatilization potential; determine well design parameters, e.g., screened interval	R	ASTM D4750; ASTM D5092; ASTM D5220; ASTM D5730; ASTM D5778; ASTM D6000; ASTM D6067; Freeze and Cherry, 1979; Benson <i>et al.</i> , 1984
Location of ground water recharge/dis- charge areas (e.g., lakes, streams, canals, retention ponds, catch basins, ditches, tidally influenced zones)	Identify using field observations; piezocone dissipation measurements to determine piezometric surface; imultiple level monitoring wells	Identify, when coupled with geochemical data, areas of natural ground water aeration, nutrient introduction, and contaminant discharge to potential receptors	R	ASTM D3385; ASTM D5092; ASTM D5730; ASTM D5778; ASTM D6067; ASTM E1689; EPA 1993a and b; Freeze and Cherry, 1979

Table 4. Hydrogeological Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES
Aquifer thickness	Measure in the field using geophysical properties; piezocone lithologic and dissipation measurements; soil borings	Estimate volatilization potential and model ground water flow; determine screened interval and other well design parameters		ASTM D5778; ASTM D6067; Benson <i>et al.</i> , 1984; Nielsen, 1991
Vadose zone permeability	Measure using permeameters; tensiometers; evaluate soil moisture content and characteristic curves to determine unsaturated permeability	Estimate contaminant migration potential; determine whether or not contaminants can or have migrated from the vadose zone to an aquifer; determine whether contaminants pose an air hazard	0	ASTM D2434; ASTM D3385; EPA 1993a and b; Everett <i>et al.</i> , 1984; Wilson <i>et al.</i> , 1995
Precipitation, tidal influence, and seasonal water table fluctuations	Measure in the field using monitoring wells; piezocone; geophysical properties; consult meterological data base http://www.ncdc.noa a.gov/	Estimate size and source of smear zone; estimate mixing zone characteristics; evaluate variability of contaminant concentrations, variation in flow direction, naturally induced volatilization potential, and nutrient introduction zones	0	ASTM D 2434; ASTM D3385; ASTM D4750; ASTM D5092; ASTM D5093; ASTM D5778; ASTM D6000; ASTM D6067
Grain size distribution	Measure using sieve analyses; hygrometers	Estimate porosity, unsaturated and saturated hydraulic conductivity, partition coefficients (in some cases), select screened interval, i.e., coarse grained sediment	0	AGI, 1989; ASTM D421; ASTM D422; ASTM D1140; ASTM D2217; ASTM D5092

Table 4. Hydrogeological Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES
Soil bulk density	Measure using cone penetration tests; drive cylinder tests; geophysical properties; sand-cone method; laboratory fluid displacement tests	Estimate groundwater velocity; essential model input parameter	0	AGI, 1989; ASTM D854; ASTM D1556; ASTM D2167; ASTM D4564
Soil porosity	Measure laboratory pore volume and specific retention	Estimate ground water velocity; essential model input parameter	0	AGI, 1989; ASTM D854; ASTM D1556; ASTM D4404

Table 5. Biogeochemical Data. This table presents data related to biotic processes that affect contaminants. Parameters that are usually required are identified with a "R" and parameters that are site specific are identified with an "O". Some parameters are collected as a research effort and are identified as "R&D". Figure 1 illustrates some of the biogeochemical zones referred to in this table.

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES
Dissolved O ₂ (D.O.) levels upgradient of the source and inside and outside of the plume	Performed in the field using an oxygen electrode or field titration kit	Define aerobic and anaerobic regions of the contaminated site; determine if sufficient D.O. is present for aerobic biodegradation (> 0.5 mg/L) which is generally faster for fuel hydrocarbons than anaerobic degradation; determine if reductive dehalogenation or aerobic oxidation of vinyl chloride or dichloroethene is feasible	R	ASTM D888; ASTM D1252; ASTM D5463
Redox potential	Performed in the field using a redox electrode	Indicator of the contaminated site conditions; negative redox potential suggests anaerobic degradation; highly negative redox potentials are required for methanogenesis and PCE/TCE degradation	R	ASTM D1498; ASTM E1196

Table 5. Biogeochemical Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES
Methyl-t-butyl ether (MTBE), Trimethyl benzene (TMB), Ethylene dibromide (EDB) and ethylene dichloride (EDC)	Require samples for laboratory analysis	Used as conservative tracers; TMB is used to calculate degradation rates; EDB and EDC indicate leaded gasoline	0	EPA 1993c
Bacterial enumeration	Requires samples for laboratory analysis using plate counts, most probable number (MPN), microscopy	Determine if contaminant degrading bacteria are present in sufficient numbers to remediate the site; more critical for chlorinated solvent sites than hydrocarbon sites	0	Harriott and Cornish-Frazer, 1997
Soil gas oxygen concentration and rate of oxygen consumption in the vadose zone	Performed in the field using an oxygen electrode	Define aerobic versus anaerobic conditions in the vadose zone; aerobic degradation requires > 1 - 2% oxygen by volume; rate of oxygen consumption can be used as an indirect measure of the biodegradation rate	O	ASTM D4478; ASTM D5314; Nielsen, 1991; Wilson et al., 1995

Table 5. Biogeochemical Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES
Carbon dioxide in the vadose and saturated zones	Performed in the field using a carbon dioxide sensor	Evaluate configuration of the dissolved plume; increased levels of carbon dioxide suggest degradation is occurring; depletion of carbon dioxide in anaerobic zones is associated with methanogenesis	O	ASTM D513; ASTM D5314; ASTM D5463; EPA 1993c; Wilson et al., 1995
Carbonate alkalinity/hard- ness	Requires samples for laboratory analysis using ion chromatography (IC) and titration	Increased carbonate concentrations may be associated with soluble contaminants, i.e., bacterial metabolism of soluble contaminants generates carbon dioxide	0	ASTM D511; ASTM D1067; ASTM D1126; ASTM D3875; ASTM D5463
Hardness - other than carbonate, e.g., calcium and magnesium	Requires samples for laboratory analysis using IC	Identify increased hardness regions which may correspond to soluble contaminant plumes; microbial production of carbon dioxide may solubilize calcium and magnesium	0	ASTM D511; ASTM D1126; ASTM D5463
Organic carbon content	Requires samples for laboratory analysis using an organic carbon analyzer	Estimate partition coefficients; evaluate contaminant retardation potential; determine if there is adequate carbon to support the degradation of TCE and PCE	0	ASTM D 2579; ASTM D4129; ASTM D4779

Table 5. Biogeochemical Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES	
pH Performed in the field using a pH electrode		Identify reduced pH regions due to carbon dioxide production which may correspond to soluble contaminant plumes; alternatively increased pH regions may indicate that electron acceptors other than oxygen are being utilized; the optimum pH for bioremediation is 4 – 9; consistent pH suggests aquifer connectivity	0	ASTM D1067; ASTM D1293; ASTM D2976; ASTM D4980; ASTM D4972; ASTM D5128; ASTM D5463; ASTM P228; EPA 1993c	
Salinity Performed in the field using a conductivity meter		Elevated salinity may reduce microbial activity	0	ASTM D512; ASTM D1125; ASTM D2791; ASTM D4458	
Temperature Performed in the field using a thermometer or thermocouple		Optimal soil and water temperatures are 10° to 40° C	0	EPA, 1993c	
Dissolved Fe(II) - ferrous iron and oxidized Fe(III) - ferric iron Fe(III) can be analyzed in the field, Fe(III) is analyzed in the laboratory using IC, AA, ICP, XRF		Identify conditions that facilitate iron reduction driven degradation pathways	0	ASTM D 1068; ASTM D1976; ASTM D4190; ASTM D4691; ASTM D5463; EPA 1993b	
Phosphorus	Can be analyzed in the field or laboratory using IC	Phosphorus is an essential nutrient; concentrations of phosphate less than 100 ppb may be limiting	0	EPA 1993c	

Table 5. Biogeochemical Data (Continued)

PARAMETER METHOD A		APPLICATION	DATA QUALIFIER	REFERENCES	
Methane	Determined in the field using a vapor analyzer equipped with a carbon tip or in the lab using GC	Indicator of anaerobic degradation (when used in conjunction with other indicators, e.g., redox potential < - 400mv and absence of oxygen	0	ASTM D5314; EPA 1993c	
Nitrogen as ammonia, nitrate, nitrite	as Performed in the Evaluate a, field using ion- configuration of t		0	ASTM D3867; ASTM D5463; EPA 1993b and c	
Sulfate	Performed in the field or laboratory using colorimetry or IC	Evaluate the extent of the dissolved plume; anaerobic degradation is occurring if sulfate is reduced to sulfide	0	ASTM D516; ASTM D4130; ASTM D4658; ASTM D5463; EPA 1993b and c	
Additional ions Na ⁺ , K ⁺ , Cl ⁻ , Mn ⁺²	Some can be analyzed in the field with ion specific electrodes or field kits or sent to the lab for analysis using AA, XRF, IC, ICP	Essential nutrients; indicators of biogeochemical processes, e.g., chloride and the degradation of TCE/PCE; manganese driven degradation if the concentration of Mn ⁺² increases; mass balances of Na ⁺ , K ⁺ , Cl ⁻ , used for quality control of data	O	EPA 1993a,b, and c	

Table 5. Biogeochemical Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIER	REFERENCES
Vadose and saturated zone microcosms	Samples collected for treatability studies	Determine if organisms indigenous to the site degrade the contaminants; evaluate abiotic mechanisms	O	ASTM D932; ASTM D3862; ASTM D3863 ASTM D3870; ASTM D4012; ASTM D4412; ASTM D4454; ASTM D4455; ASTM D5245; ASTM E1196; ASTM E1197; ASTM E1525; ASTM F488; Chappelle, 1993; Wilson et al., 1995; Wiedemeier, et al, 1995; NRC, 1993; Smith et al., 1986
Dissolved hydrogen	Samples are sent to the laboratory	Evaluate the potential for microbial degradation of chlorinated compounds; identify the predominant terminal electron accepting process (for DNAPLs) based on the hydrogen concentrations in Table 1	R&D	Chappelle et al., 1996
¹² CO ₂ / ¹³ CO ₂	Requires samples for laboratory analysis using GC/MS	Evaluate stable isotopes of carbon to monitor biodegradation of pollutants; an increase in the ratio ¹² C/ ¹³ C suggests that biodegradation is occurring	R&D	ASTM D5314; ASTM D5463
Bacterial ribosomal RNA	Requires samples for laboratory analysis using PCR	Identify bacteria associated with the degradation of specific contaminants and measure bacterial population density	R&D	Braun-Howland, et al., 1993; Guschin et al., 1997; Liu et al., 1997
Bacterial cell components (lipid fatty acids, respiratory activity, enzymes)	Requires samples for laboratory analysis using enzymological assays and GC	Determine bacterial population density, types of bacteria, activity and viability of indigenous bacteria	R&D	Frostegard et al., 1993; Posch et al., 1997; Roslev and King, 1993; Sorensen and Ahring, 1997; Smith, et al., 1986

Table 6. Contaminant Data. This table presents parameters that aid in identifying contaminants, defining the extent of the contamination, and status of the plume. Parameters that are usually required are identified with an "R" and parameters that are site specific are identified with an "O". Data that are normally collected as part of a research and development effort are identified with "R&D".

PARAMETER	METHOD	APPLICATIO N	DATA QUALIFIER	REFERENCES
Delineation of contaminant source and concentration; extent of the soluble plume	Derived by mapping concentration data superimposed on site map	Determine in conjunction with time series and/or modeling if the plume is stable, expanding or contracting; high concentrations of contaminants may be toxic to microorganisms	R	ASTM DFS; ASTM D420; ASTM D4448; ASTM D4700; ASTM D5730; ASTM D5851; ASTM D5903; ASTM D6000; ASTM D6001; ASTM D6044; ASTM D 6051; ASTM E943; ASTM E978; ASTM PS3; ASTM P64; ASTM P85; Everett et al., 1984; EPA 1993a, b, c, and d; Freeze and Cherry, 1979; Nielsen, 1991; Pankow and Cherry, 1996; Wilson et al., 1995; Bardossy, 1992, Knowles, et al., 1997
Presence of free product	Determined in the field using ullage meter, reactive tape, bailer, direct-push sampler, direct-push video microscope	Determine whether free- product has to be removed	R	Nielsen, 1991
Type(s) of contaminant(s)	Historical records; results of field and lab analyses	Select appropriate site characterization and monitoring tools; evaluate chemical phases: soluble, vapor, liquid; estimate fate and transport of the contaminants	R	ASTM DFS; ASTM D5463; ASTM D6030; ASTM P85; EPA, 1993a,b,c, and d
Parent contaminants and intermediates	Historical records and analytical results	Determine extent of biotic and abiotic weathering	0	EPA, 1993a,b, and c
Date of contaminant release	Historical records and estimates made from site assessment data, e.g., rate of groundwater movement, inverse modeling	Estimate expected extent of plume migration; determine velocity of contaminant migration	0	Nielsen, 1991

Table 6. Contaminant Data (Continued)

PARAMETER	METHOD	APPLICATION	DATA QUALIFIE R	REFERENCES
Volume of contaminant release	Historical records and estimates made from site assessment data	Estimate expected size and extent of plume migration	0	EPA, 1988; Gilbert, 1987; Nielsen, 1991
Rate of contaminant release	Historical records	Estimate expected extent of plume migration	0	Nielsen, 1991
Dispersion coefficients Field measurements or correlations with lithology		Essential model parameter; evaluate contaminant fate, transport, and concentration distribution	0	Nielsen, 1991
Partition coefficients of contaminant components	Use published data, Henry's Law, Raoult's Law or results from site assessment	Evaluate contaminant phase, i.e., adsorbed, gaseous or soluble, fate and transport retardation; essential fate and transport model parameter	0	ASTM D4646; ASTM E1147; ASTM E1148; ASTM E1195; Roy, et al., 1992
Time series of contaminant historical records, plume (i.e. concentration the analysis of state, decrease)		Evaluate status of plume (i.e., steady state, decreasing, migrating)	0	ASTM D5447; ASTM D5490; ASTM D5609; ASTM D 5610; ASTM D5611; ASTM D5714; ASTM D5718; ASTM D5719; ASTM D5880; ASTM PS64; EPA, 1988; Gilbert 1987, Nielsen, 1991
Biodegradation rates of contaminant components	Use published data or results from site assessment	Evaluate rate of contaminant destruction to determine whether natural attenuation is a feasible and practical solution under site specific conditions; input for fate and transport models	R&D	Howard, et al., 1991, McAllister and Chiang, 1994; NRC, 1993

Table 7. Direct Push Tools. This table presents direct push methods that are increasingly used to rapidly and economically perform a site evaluation, collect samples, and install monitoring wells (Meuzelaar, H.L.C, 1998).

TOOL	APPLICATION			
Laser Induced Fluorescence (LIF)	Delineate hydrocarbon plume and monitor changes in the plume configuration; identifying shifts in emission spectra towards longer wavelengths can potentially indicate hydrocarbon degradation (experimental).			
Cone pressure and sleeve friction	Characterize lithology; identify preferential flow pathways and confining layers.			
Water sampler	Collect confirmation samples; plume delineation; determine pore water characteristics (chemistry, temperature, conductivity, redox potential).			
Micro-well	Collect confirmation samples; plume delineation; determine pore water characteristics (chemistry, temperature, conductivity, redox potential); determine hydrogeologic parameters (direction of flow, hydraulic conductivity, storativity); introduce monitoring devices.			
Moisture probe (time domain reflectometry) and conductivity	Determine unsaturated hydraulic conductivity (when coupled with soil characteristic curve); identify location of ionic fronts (saltwater intrusion, river recharge, infiltration).			
Video microscope	Determine grain size distribution; estimate permeability and hydraulic conductivity; identify preferential flow paths, confirmation of cone pressure and sleeve friction lithologic interpretation; detect free-phase non-aqueous phase liquid (experimental).			
Soil gas sampler	Detect VOCs, fixed and biogenic gases; determine air flow rates; determine respiration rate.			
Piezocone	Determine pore pressure; delineate stratigraphic profile; estimate site hydrogeologic conditions (permeability, water table elevation, direction and gradient of subsurface water flow); identify confining zones; identify potential zones of vertical migration; select optimal water sampling zones; identify zones of aquifer communication; identify candidate receptors.			
Laser Induced Breakdown Spectroscopy (LIBS)	Detect metal contaminants in soil.			
Ground Water Modeling Software (GMS), Global Positioning System (GPS), Autocad	Display conceptual models; integrate geologic and chemical mapping; model ground water and chemical fate and transport.			

REFERENCES

ASTM Standards

- DFS Draft standard guide for selection of chemical field screening and field analytical methods used in vadose zone investigations.
- DNA Draft standard guide for remediation of ground water by natural attenuation at petroleum release sites.
- D 420 Guide for investigating and sampling soil and rock.
- D 421 Practice for dry preparation of soil samples for particle-size analysis and determination of soil constants.
- D 422 Method for particle-size analysis of soils.
- D 511 Test methods for calcium and magnesium in water.
- D 512 Test methods for chloride ion in water.
- D 513 Test methods for total and dissolved carbon dioxide in water.
- D 516 Test method for sulfate ion in water.
- D 854 Test method for specific gravity of soils.
- D 888 Test methods for dissolved oxygen in water.
- D 932 Test method for iron bacteria in water and water-formed deposits.
- D 1067 Test methods for acidity or alkalinity of water.
- D 1068 Test methods for iron in water.
- D 1125 Test methods for electrical conductivity and resistivity of water.
- D 1126 Test methods for hardness of water.
- D 1140 Test method for amount of material in soils finer than the no200 sieve.
- D 1252 Test method for chemical oxygen demand (dichromate oxygen demand) of water.
- D 1293 Test methods for pH of water.

- D 1452 Practice for soil investigation and sampling by auger borings.
- D 1498 Practice for oxidation-reduction potential of water.
- D 1556 Test method for density and unit weight of soil in-place by the sand-cone method.
- D 1586 Method for penetration test and split-barrel sampling of soils.
- D 1587 Method for thin-walled tube sampling of soils.
- D 1976 Test method for elements in water by inductively-coupled argon plasma atomic emission spectroscopy.
- D 2167 Test method for density and unit weight of soil in-place by the rubber balloon method.
- D 2216 Test method for laboratory determination of water (moisture) content of soil and rock.
- D 2217 Practice for wet preparation of soil samples for particle-size analysis and determination of soil constants.
- D 2325 Test method for capillary-moisture relationships for coarse and medium-textured soils by porous-plate apparatus.
- D 2434 Test method for permeability of granular soils (constant head).
- D 2488 Practice for description and identification of soils (visual-manual procedure).
- D 2579 Test methods for total and organic carbon in water.
- D 2791 Test method for continuous determination of sodium in water.
- D 2976 Test method for pH of peat materials.
- D 3017 Test method for moisture content of soil and rock in-place by nuclear methods.
- D 3152 Test method for capillary-moisture relationships for fine-textured soils by pressure-membrane apparatus.
- D 3385 Test method for infiltration rate of soils in field using double-ring infiltrometers.
- D 3404 Standard guide for measuring matric potential in the vadose zone using tensiometers.
- D 3862 Test method for retention characteristics of 0.2 micrometer membrane filters used in routine filtration procedures for the evaluation of microbiological water quality.

D 3863 Test method for retention characteristics of 0.4 to 0.45 micrometer membrane filters used in routine filtration procedures for the evaluation of microbiological water quality.

D 3867 Test method for nitrite-nitrate in water.

D 3870 Practice for establishing performance characteristics for colony counting methods in bacteriology.

D 3875 Test method for alkalinity in brackish water, sea water, and brines.

D 4012 Test method for adenosine triphosphate (ATP) content of microorganisms in water.

D 4043 Standard guide for selection of aquifer-test method in determining of hydraulic properties by well techniques.

D 4044 Standard test method for (field procedure) for instantaneous change in head (slug tests) for determining hydraulic properties of aquifers.

D 4050 Standard test method (field procedure) for withdrawal and injection well tests for determining hydraulic properties of aquifer systems.

D 4075 Test method for determination of metals using flame atomic absorption techniques.

D 4083 Practice for description of frozen soils (visual-manual procedure).

D 4129 Test method for total and organic carbon in water by high-temperature oxidation and coulometric detection.

D 4130 Test method for sulfate ion in brackish water, seawater, and brines.

D 4190 Test method for elements in water by direct-current argon plasma atomic emission spectroscopy.

D 4220 Practice for preserving and transporting soil.

D 4404 Test method for determination of the pore volume and pore volume distribution of soil and rock by mercury intrusion porosimetry.

D 4412 Test methods for sulfate-reducing bacteria in water and water-formed deposits.

D 4448 Guide for sampling ground water monitoring wells.

D 4454 Test method for simultaneous enumeration of total respiring bacteria in aquatic systems by microscopy.

D 4455 Test method for enumeration of aquatic bacteria by epifluorescence microscopy counting procedure.

D 4458 Test method for chloride ions in brackish water, seawater, and brines.

D 4478 Test methods for oxygen uptake.

D 4564 Test method for density of soil in-place by the sleeve method.

D 4643 Method for determination of water (moisture) content of soil by the microwave oven method.

D 4646 Method for 24-hour batch-type measurement of contaminant sorption by soils and sediments.

D 4658 Test method for sulfide ion in water.

D 4691 Practice for measuring elements in water by flame atomic absorption spectrophotometry.

D 4700 Guide for soil sampling from the vadose zone.

D 4750 Standard test method for determining subsurface liquid levels in a borehole or monitoring well (observation well).

D 4779 Test method for total organic and inorganic carbon in high purity water by ultraviolet (UV) or persulfate oxidation, or both, and infrared detection.

D 4839 Test method for total carbon and organic carbon in water by ultraviolet (UV) or persulfate oxidation, or both, and infrared detection.

D 4944 Test method for field determination of water (moisture) content of soil by the calcium carbide gas pressure tester method.

D 4959 Test method for determination of water (moisture) content of soil by direct heating method.

D 4972 Test method for pH of soils.

D 4980 Method for the screening of pH in wastes.

D 5084 Test method for hydraulic conductivity of saturated porous materials using a flexible wall permeameter.

D 5092 Practice for design and installation of ground water monitoring wells in aquifers.

- D 5093 Test method for field measurement of infiltration rate using a double-ring infiltrometer with a sealed inner ring.
- D 5126 Guide for comparison of field methods for determining hydraulic conductivity on the vadose zone.
- D 5128 Test method for on-line pH measurement of water of low conductivity.
- D 5220 Test method for water content of soil and rock in-place by the neutron depth probe method.
- D 5245 Practice for cleaning laboratory glassware, plasticware, and equipment used in microbiological analyses.
- D 5298 Test method for measurement of soil potential (suction) using filter paper.
- D 5314 Guide for soil gas monitoring in the vadose zone.
- D 5434 Guide for field logging of subsurface explorations of soil and rock.
- D 5447 Guide for application of a ground water flow model to a site specific problem.
- D 5463 Guide for use of test kits to measure inorganic constituents in water.
- D 5490 Guide for comparing ground water flow model simulations to site specific information.
- D 5609 Guide for defining boundary conditions in ground water flow modeling.
- D 5610 Guide for defining initial conditions in ground water flow modeling.
- D 5611 Guide for conducting a sensitivity analysis for a ground water flow model application.
- D 5714 Specification for content of digital geospatial metadata.
- D 5718 Guide for documenting a ground water flow model application.
- D 5719 Guide to simulation of subsurface air flow using ground water flow modeling codes.
- D 5730 Standard Guide for site characterization for environmental purposes with emphasis on soil, rock, the vadose zone and groundwater.
- D 5778 Test method for performing electronic friction cone and piezocone penetration testing of soils.
- D 5851 Guide for planning and implementing a water monitoring program.

- D 5880 Guide for subsurface flow and transport modeling.
- D 5903 Guide for planning and preparing for a ground water sampling event.
- D 6000 Guide for the presentation of water-level information from groundwater sites.
- D 6001 Guide for direct push water sampling for geoenvironmental investigations.
- D 6030 Guide to selection of methods for assessing ground water or aquifer sensitivity and vulnerability.
- D 6044 Guide for representative sampling and management of waste and contaminated media.
- D 6051 Guide for composite sampling and field subsampling for environmental waste management activities.
- D 6067 Guide for using the electronic cone penetrometer for environmental site characterization.
- E 943 Terminology relating to biological effects and environmental fate.
- E 978 Practice for evaluating environmental fate models of chemicals.
- E 1147 Test method for partition coefficient (n-octanol/water) estimation by liquid chromatography.
- E 1148 Test method for measurement of aqueous solubility.
- E 1195 Test method for determining a sorption constant (koc) for an organic chemical in soil and sediments.
- E 1196 Test method for determining the anaerobic biodegradation potential of organic chemicals.
- E 1197 Guide for conducting a terrestrial soil-core microcosm test.
- E 1525 Guide for designing biological tests with sediments.
- E 1599 Standard guide for corrective action for petroleum releases.
- E 1689 Standard guide for developing conceptual site models for contaminated sites.
- E 1739 Standard guide for risk-based corrective action applied at petroleum release sites.
- F 488 Test method for total bacterial count in water.
- P 228 Proposed test methods for pH measurement of water of low conductivity.

PS 3 Provisional standard guide for accelerated site characterization for confirmed or suspected petroleum releases.

PS 64 Provisional standard guide for developing appropriate statistical approaches for ground water detection monitoring programs.

PS 85 Provisional guide for expedited site characterization of hazardous waste contaminated sites.

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